TITLE

SYSTEM AND METHOD FOR PROTECTING METALS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Serial No. 60/403,859 (filed August 15, 2002), which is incorporated by reference herein for all purposes as if fully set forth.

BACKGROUND OF THE INVENTION

This invention pertains to the protection of metals from corrosion and/or fouling from exposure to environments such as, for example, seawater. The protection in accordance with this invention is achieved through the use of conductive zinc-containing coatings in combination with applied current cathodic protection.

Cathodic protection is a traditional electrochemical technology that can be used to protect metallic materials from corrosion in electrolytic environments. When a metal is immersed in an electrolytic environment, such as seawater, the metal corrodes because numerous microelectrochemical cells are established on the surface. Generally speaking, these electrochemical cells are composed of two reactions - the anodic reaction that oxidizes metal to form metallic ions dissolved in the electrolyte, and the cathodic reaction that reduces oxygen to form hydroxyl ions. When metal is freely immersed in the electrolytic solution, these two reactions proceed at the same rate, but the final consequence of these reactions is the corrosion of metal. However, if an external cathodic current is applied to this freely immersed metal by using another auxiliary electrode, these two reactions on the metal surface will lose balance. The anodic reaction that causes the dissolution of metal will be retarded and the cathodic reaction will be increased.

Theoretically, the anodic reaction, or the corrosion of metal, can be totally stopped by this applied cathodic current. The technology that uses the cathodic current to reduce the corrosion of metal is called cathodic protection. Cathodic current can be applied to a metal by two well-known ways.

One way (the applied current cathodic protection system) utilizes an external cathodic current that is applied to the metal via a D.C. power source using an auxiliary electrode as anode.

Another way (the sacrificial anode cathodic protection system) uses a sacrificial anode that is directly connected to the metal to be protected. The sacrificial anode has a more negative potential than that of the metal, thus a battery is formed between the metal and the sacrificial anode that supplies the cathodic current. The most widely used sacrificial anodes are made of magnesium or aluminum.

In the design of cathodic protection systems, the following issues need to be addressed:

(1) The amount of cathodic current applied is dependent on the total surface area of metal to be protected. In order to save electricity, cathodic protection is usually used in conjunction with organic coatings. The result is that, when the organic coating is newly applied and intact, corrosion protection primarily comes from the coating, while the cathodic protection system remains idle because the metal is insulated from the environment by the organic coating. When the coating becomes degraded and some of the bare metal surface is exposed to the environment, cathodic protection begins to work to protect the exposed surface area.

(2) If the amount of cathodic current applied is too much, hydrogen evolution (or reduction) can occur. The evolved hydrogen will prematurely damage the coating system, and may cause embrittlement of the underlying metal.

(3) The auxiliary anode generally dissolves very fast; therefore, the anode has to be made from a specially designed alloy.

Fouling is also a common problem in water environments. Various antifouling methods have been described in the literature, and the most commonly used methods involve the application of a coating or other layer containing additives that are toxic to marine life. Biocides such as tin compounds are prevalent and effective, but their future use is in doubt due to stricter environmental regulation.

Zinc has found widespread use as a sacrificial anode, and is commonly applied as a zinc-rich coating. Zinc is a cost-effective material, has effective biocide properties for reducing fouling from sources such as marine organisms, and is a more environmentally acceptable material than the current tin-based products. Zinc-containing coatings, and particularly zinc-rich coatings, are in general well-known as protective coatings, and are widely used in a variety of industries including marine, automotive and construction.

In view of the principles of the sacrificial anode cathodic protection system, it is not difficult to understand the protection mechanism of zinc-containing coatings. In such coatings, numerous micro-sacrificial zinc anodes (zinc particles) are in electrical contact with the metal surface. In corrosive environments, zinc particles are preferentially corroded while the metal surface is cathodically protected. In order to have sufficient cathodic protection properties, "zinc-rich" coatings are used, which contain a large amount of zinc particles to ensure that enough electrical contact between the metal surface and zinc particles can be established. Zinc-rich coatings can be organic (e.g., contain organic components such as

polymeric binders) or inorganic, with the zinc content (solids) being generally more than 80% by weight, and usually more than 95% in weight.

Although the corrosion protection functionality needs a high content of zinc, the high content of zinc also unfortunately imparts zinc-rich coatings with many inferior properties. For example, zinc-rich coatings usually have poor adhesive properties and are very brittle (especially for inorganic coatings). In addition, the zinc-rich coating film itself is easily corroded and, therefore, needs a top coating as a barrier to provide additional protection.

It would, therefore, be desirable to find a system that effectively utilizes the corrosion protection of coatings, and corrosion protection and anti-fouling properties of zinc.

US4196064 discloses a system for controlling marine fouling by coating a metal substrate on the exposed side with a coating containing stainless steel particles then, in the exposure environment, impressing an electrical potential to the coated substrate such that the exposed surface (coating) is cathodic. A zinc-rich undercoating may be used in this system to provide additional corrosion protection to the underlying substrate, but such zinc coating is not intended to be exposed to the environment.

US5005165, US5009757, US5346598 and US5643424 all disclose an anti-fouling system in which a zinc-rich inorganic paint is applied to the exposed side of a steel hull. The zinc coating forms an interfacial layer between the seawater and the ship's hull. One or more titanium electrodes are disposed within the ship's hull (on the other side of the ship hull and separated from the water side). These titanium electrodes are protected from contact by the water. The titanium electrodes are mounted on insulators within a conductive hollow body filled with a liquid electrolyte. The hollow body is secured to the ship's hull by a conductive mount. A power supply is connected to the titanium electrode and the conductive surface of the ship's hull. The positive terminal of the power supply is connected to the titanium rod external to the hollow body and the negative terminal is connected to the ship's hull. The system is said to impose a negative capacitive charge to the surface of the exposed zinc coating.

In this system, however, the electrons from the negative terminal of the power supply go through the ship's hull (conductive), hollow body (conductive), interface of hollow body/electrolyte, electrolyte, interface of titanium/electrolyte, and titanium (conductive), and return to the positive terminal to form a close circuit. The electrochemical reactions can thus occur only on two interfaces - the titanium/electrolyte and hollow body/electrolyte – and the described orientation of

components should not have any effect on the electrochemical reactions (corrosion and/or fouling) occurring on the exterior surface (zinc coated surface) of the ship's hull. Since the cathode in this system is actually the hollow body in contact with the electrolyte, the consequence of using this apparatus is that the corrosion of the hollow body will be reduced due to the cathodic protection received and the corrosion of titanium electrode will be increased. Again, it is not clear how this system would have any effect, detrimental or beneficial, on the corrosion/or fouling of the ship's hull.

All of the above-identified publications are incorporated by reference herein for all purposes as if fully set forth.

SUMMARY OF THE INVENTION

In accordance with one aspect of the present invention, there is provided a method for protecting a metal structure from corrosion and/or fouling, said metal structure comprising a metal which has a higher electrochemical potential than zinc, and an exposure surface exposed to an environment conducive to corroding and/or fouling said metal, said exposure surface being at least partially coated with a conductive zinc-containing coating in conductive contact with said metal and in direct contact with said environment, said method comprising the step of applying a direct current through said conductive zinc-containing coating via a resistive circuit in which said metal functions as a cathode.

In accordance with another aspect of the present invention, there is provided an improved method for protecting a metal structure from corrosion and/or fouling by applied current cathodic protection, said metal structure comprising a metal which has a higher electrochemical potential than zinc, and an exposure surface exposed to an environment conducive to corroding and/or fouling said metal, wherein the improvement comprises providing at least a part of said exposure surface with a conductive zinc-containing coating such that said zinc-containing coating is conductive contact with said metal and in direct contact with said environment, and applying a direct current through said conductive zinc-containing coating via a resistive circuit in which said metal functions as a cathode.

In accordance with yet another aspect of the present invention, there is provided a system for protecting a metal structure from corrosion and/or fouling, said metal structure comprising a metal which has a higher electrochemical potential than zinc, and an exposure surface exposed to an environment conducive to corroding and/or fouling said metal, said system comprising:

(1) a conductive zinc-containing coating on at least a part of said exposure surface, said conductive zinc-containing coating being in conductive contact with said metal and in direct contact with said environment;

(2) a direct current supply having a positive terminal and a negative terminal; and

(3) a resistive circuit connecting said positive and negative terminals, said resistive circuit comprising said metal as a cathode and an anode resistively connected thereto, and wherein said resistive circuit is structured so that a direct current will flow through said conductive zinc-containing coating.

In each of the aforementioned aspects, it is generally preferred that the exposure surface is substantially covered with the conductive zinc-containing coating. It is also (or alternatively) generally preferred that the resistive circuit comprises the metal as the cathode, and an anode in the exposure environment. In another preferred embodiment, the zinc-containing coating is a zinc-rich coating. Alternatively, it yet another preferred embodiment, the zinc-containing coating can have a lower zinc content and a higher content of binder matrix and other additives to impart a variety of advantageous physical and/or chemical properties to the zinc-containing coating (in comparison to zinc-rich coatings).

The methods and systems in accordance with the present invention are advantageous in that the zinc in the conductive zinc-containing coating is cathodically protected via the applied current and, therefore, is resistant to rapid corrosion, thereby alleviating the need for protective topcoats commonly used when zinc-rich layers are present. Because the zinc is protected from corrosion, the conductive zinc-containing coating maintains its integrity better and substantially longer, and thus actually can function as a protective coating for the underlying metal. The underlying metal is thus protected via three mechanisms in a simplified system - the metal is cathodically protected via the applied current, the metal is cathodically protected by the zinc which can still function as a sacrifical anode, and the metal is physically protected by the zinc-containing coating which now can function as a protective coating. In addition, since the zinc is not as rapidly corroded in the present system, it remains available as an anti-fouling agent.

The methods and systems in accordance with the present invention find use in numerous well-known fields where corrosion and/or fouling are a concern, a primary example of which is in the protection or ships and other metallic structures (such as bridges, storage tanks, pipelines and structural steel) exposed to seawater or other brackish water sources.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description. It is to be appreciated that certain features of the invention which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cross-sectional view of a section of a structural member exposed to a corrosive and/or fouling environment having a conductive zinc-containing coating adhered thereto.

FIG. 2 is a schematic side view of an ocean vessel having the system of the present invention aboard.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIG. 1, a metal substrate 1, such as a ship's hull, is shown to be coated with a conductive zinc-containing coating 3.

Suitable zinc-containing coatings for use with the present invention must, of course, contain zinc (and/or a zinc oxide), and be conductive in the sense that a current will flow from an anode, through the zinc-containing coating and to the cathode (metal). These types of coatings are in general well-known to those of ordinary skill in the art.

In one preferred embodiment, the zinc-containing coating is a zinc-rich coating, as that term is commonly understood by those of ordinary skill in the art. See, for example, "Surface Coatings, Volume 1: Raw Materials and Their Usage", P. Parsons, Chapman & Hall (London), 1993, pp 412, 423. Zinc-rich coatings typically comprise a high zinc loaded inorganic or organic polymer matrix. Typical zinc loadings are in excess of 80% by weight based upon solids, and most often in excess of 85% by weight. Such coatings are commercially available from numerous sources.

Solvent-borne inorganic zinc-containing coatings with alkyl silicate binders include, for example, Ganicin 347YV912 (E.I. duPont de Nemours and Company) and Carbozinc 11 (Carboline).

Solvent-borne organic zinc-containing coatings with epoxy binders include Ganicin 347Y937 (E.I. duPont de Nemours and Company) and Carbozinc 859 (Carboline).

Waterborne inorganic zinc-containing coatings with potassium silicate binders include Carbozinc 11 (Carboline).

Solvent-borne organic zinc-containing coatings with 2K urethane binders include 62ZF (E.I. duPont de Nemours and Company).

The preferred coatings for this invention are the inorganic silicate types where conductivity is better than the organics that may tend to encapsulate and insulate more of the zinc particles.

The metals to be protected are those that have a higher electronegative potential than zinc, most notably iron and iron-based alloys such as steel.

For best results, it is preferred that the entire exposure surface of the metal be substantially coated with the zinc-containing coating.

In FIG. 2, an ocean vessel 10 is shown floating on the surface of the water 2 and having the system of the invention aboard. DC generator 5 generates a cathode and an anode potential. DC generator 5 is connected via electrical conductor 8 to a connector to the hull of the ship 9 such that the hull is cathodic upon operation of the generator. DC generator 5 is also connected via insulated electrical conductors 7 to impressed current anodes 6 which are electrically insulated from the hull 9 and which are located in distribution thereover. Upon operation of DC generator 5, a circuit is formed as current flows from the positive terminal of DC generator 5 through anodes through electrolytic environment (such as sea water), through the zinc-containing coating which covers parts of the hull 9 exposed to fouling (coating not shown in this figure), through hull 9 to the conductors 7 and back to the negative terminal of DC generator 5.

The circuit so formed is resistive so as to avoid a short circuit in the system. The resistivity can arise from a number of aspects. For example, since the anodes 6 are electrically insulted from the hull 9, the current will flow through seawater. The zinc-containing coating, although conductive, may also add resistance to the system, particularly depending on zinc and other conductive component content. These and other aspects of the formed circuit are readily discernible by those of ordinary skill in the art.

Normally, an electrical voltage is employed such that the cathodic current density is between about 1 mA/sq.ft to about 100 mA/sq.ft, more preferably from about 1.5 mA/sq.ft to about 35 mA/sq.ft. The negative potential shift of the cathode (or ship hull) caused by this impressed cathodic current usually is about 40 to about 400 mV. Since the zinc-containing coating already has a very negative potential, a lower cathodic current density is recommended because a high cathodic

current density will increase the undersirable evolution of hydrogen on the surface. Preferably, the electrical potential is applied substantially continuously.

In general, the various components mentioned above, such as the DC generator, anodes and conductors, are of a type well-known to those of ordinary skill in the art such as, for example, disclosed in previously incorporated US4196064.